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STUDY OF SELF-DIFFUSION IN GaAs CRYSTAL: TEMPERATURE DEPENDENCE

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Abstract. *The self-diffusion of Ga and As atoms in GaAs crystal with the zince-blende structure (ZnS) is investigated by using the statistical moment method (SMM). The activation energy (Q), diffusion coefficient (D), and pre-exponential factor (D_0) are expressed by analytical closed expressions. The present analytical formulas are including the anharmonic effects of the lattice vibrations. The obtained results are applied to GaAs crystal and the SMM calculations of Q, D and D_0 are in agreement with the experimental data.*

I. INTRODUCTION

The theory of atomic diffusion in solids has a long history [1-2]. In 1905, Einstien used the incidental chaotic model for the investigation of diffusion [1]. Bardeer and Hearing improved this model so as to include the correlation effect [3]. Using the transition state theory [4], Glestom *et al.* derived the diffusion coefficient and showed that self-diffusion obeys Arrhenius's law [5]. Kikuchi discussed the atomic diffusion in metals and alloys using the path probability method [6]. In recent years, most theoretical studies have concentrated on the investigations of self-diffusion and the diffusion of impurities in semiconductors [7,8-13].

Self-difffusion in semiconductors has been the subject of intensive research since it has an impact on many fundamental materials phenomena and is technologycally important phenomena, which has yet to be fully understood. The development of theoretical studies of atomic diffusion in Si, GaAs crystals is of great interest, not only from a fundamental, but also from a practical point of view. The most advanced theoretical studies of self-interstitials in Si, GaAs have used the local density approximation (LDA) included in density functional theory (DFT) to calculate the defect formation energy[9-10]. In general, these atomic diffusions have been studied within the framework of the simple theory of thermal lattice vibration, in which anharmonic effects are neglected. In our previous paper[2], we proposed a theoretical scheme which could be used to study the self-diffusion in metals taking into account the anharmonicity of the lattice vibration at pressure $P = 0$. In the present paper, we used the moment method in statistical dynamics to calculate the pre-exponential factor, D_0, and activation energy, Q, for self-diffusion in semiconductors.

We also compare the calculated results of D_0, and Q for GaAs crystal with the previous theoretical calculations as well as the experimental data.

II. THEORY OF SELF-DIFFUSION IN SEMICONDUCTORS

The general expression of diffusion coefficient D can be written in the form[2]

$$D = g\Gamma n_\nu r_1^2, \tag{1}$$

where r_1 is the jump distance at temperature T; g is a coefficient which depends on the crystalline structure and the mechanism of diffusion, as follows:

$$g = n_1 f, \tag{2}$$

n_1 denotes the number of Ga (or As) atoms of the first nearest neighbor from the central atom; f is the correlation factor and n_ν the equilibrium concentration of the vacancies. From the minimization condition of the Gibbs free energy of the crystal with defects, we obtain the equilibrium concentration of the vacancy as

$$n_\nu = \exp(-\frac{g_\nu^f(P,T)}{\theta}), \tag{3}$$

where $\theta = k_B T$, g_ν^f is the change in the Gibbs free energy due to the fomation of a vacancy and can be given by [2]

$$g_\nu^f = -U_0 + \Delta\psi_0^* + P\Delta V, \tag{4}$$

$$U_0 = \frac{1}{2}\sum_i \varphi_{i0}(|\overrightarrow{r}|). \tag{5}$$

Here U_0 represents the sum of the effective pair interaction energies between the 0^{th} and i^{th} atoms, and φ_{i0} the effective interaction energies between the 0^{th} and i^{th} atoms, $\Delta\psi_0^*$ denotes the change in the Helmholtz free energy of the central atom which creates the vacancy, by moving itself to a certain sink site in the crystal, and is given by

$$\Delta\psi_0^* = (B-1)\psi_0^*, \tag{6}$$

where ψ_0^* denotes the free energy of the central atom after moving to a certain sink sites in the crystal, B is simply regarded as a numerical factor. In the previous paper [14], we take the average value for B as

$$B \approx 1 + \frac{U_0}{2\psi_0^*}. \tag{7}$$

In expression (1), the attempt frequency, Γ, for atomic jumps is proportional to the transition probability of an atom

$$\Gamma = \frac{\omega}{2\pi}\exp\{\frac{\Delta\psi_1^*}{\theta}\}. \tag{8}$$

The change in the Gibbs free energy associated with the exchange of the vacancy with the neighboring atoms is equal to the inverse sign of $\Delta\psi_1^*$, and

$$g_\nu^m = -\Delta\psi_1^* = (B^{'} - 1)\psi_1^* \approx h_\nu^m, \tag{9}$$

where B' is simply regarded as a numerical factor. The factor B' is analogous to the factor B defined for formation energy of the vacancy

$$B^{'} \approx 1 + \frac{U_0 - (B-1)\psi_0^*}{2\psi_1^*}. \tag{10}$$

Since the Gibbs free energy G can be written in the form

$$G = H - TS,$$

where $S = -\left(\frac{\partial G}{\partial T}\right)_P$ is the entropy and H represent the enthalpy of the system, then the change in the Gibbs free energy g_ν^f due to the creation of a vacancy, is given by

$$g_\nu^f(P,T) = h_\nu^f(P,T) - TS_\nu^f(P,T), \tag{11}$$

with h_ν^f and S_ν^f being the enthalpy and entropy required for the formation of a vacancy, respectively. Summarizing Eqs (1)-(11), the diffusion coefficient D of a semiconductor can be derived as follows:

$$D = n_1 f \frac{\omega}{2\pi} r_1^2 \exp\{-\frac{h_\nu^f - \Delta\psi_1^*}{\theta}\} \exp\{\frac{S_\nu^f}{k_B}\}. \tag{12}$$

The above formula for the diffusion coefficient can be rewritten as

$$D = D_0 \exp\{-\frac{Q}{\theta}\}, \tag{13}$$

where

$$Q = h_\nu^f + h_\nu^m, \tag{14}$$

$$D_0 = n_1 f \frac{\omega}{2\pi} r_1^2 \exp\{\frac{S_\nu^f}{k_B}\}. \tag{15}$$

The activation energy Q is given by:

$$Q = -\frac{3}{4}U_0 + TS_\nu^f + P\Delta V, \tag{16}$$

In the case of zero pressure we obtain:

$$Q = -\frac{3}{4}U_0 + TS_\nu^f, \tag{17}$$

with the entropy for the formation of a vacancy is given by [15].

III. RESULT AND DISCUSSION

We now calculate the pre-exponential factor, D_0, activation energy, Q, and diffusion coefficient, D, for self-diffusion in GaAs semiconductor using the empirical many-body potential between the atoms Ga and As of the following equation [11]

$$\varphi = \sum_{i<j} U_{ij} + \sum_{i<j<k} W_{ijk}, \tag{18}$$

$$U_{ij} = \varepsilon[(\frac{r_0}{r_{ij}})^{12} - 2(\frac{r_0}{r_{ij}})^6], \tag{19}$$

$$W_{ijk} = Z\frac{(1+3\cos\theta_i\cos\theta_j\cos\theta_k)}{(r_{ij}r_{jk}r_{ki})^3}, \tag{20}$$

where the potential parameters ε, r_0, Z are taken from Ref. 11. These parameters are determined so as to fit the experimental lattice constants and cohesive properties.

Table 1. Potential parameters of the empirical many- body potential for GaAs [11]

$\epsilon_{AB}(eV)$	$r_{0AB}(\mathring{A})$	$Z_{AAB}(eV\mathring{A})$	$Z_{ABB}(eV\mathring{A})$	$Z_{AAA}(eV\mathring{A})$
1.738	2.448	1900.0	4600.0	1826.4

In Table 2, we present the calculated pre-exponential factor, D_0, activation energy, Q, and diffusion coefficient, D, of atoms Ga and As in GaAs crystal at the temperature range 300 K to 1500K. One sees in Table 2 that the SMM calculations of these quantities D_0, Q, and D are in good agreement with the corresponding experimental results [12]. For example, the activation energies Q calculated by SMM for diffusion As atom in GsAs lie in the range 3.1eV- 3.4eV at the temperature range 300 K to 1500K, while experimental result gives 3.2 eV.

Table 2. Present SMM calculations and experimental results of Q, D_0 and D of As, and Ga atoms in GaAs crystal.

	atoms	SMM	$Expt$[12]	$T(K)$
Q(eV)	As	$3.1 \longrightarrow 3.4$	3.2	Wide temp range
	Ga	$3.40 \longrightarrow 3.42$	2.6	$1298 \longrightarrow 1373$
			5.6	$1398 \longrightarrow 1503$
$D_0(cm^2/s)$	As	$0.34 \longrightarrow 0.40$	0.7	Wide temp range
	Ga	$0.34 \longrightarrow 0.40$	4×10^{-5}	$1298 \longrightarrow 1373$
			4×10^{7}	$1398 \longrightarrow 1503$
$D(cm^2/s)$	As	2.8×10^{-21}	4.8×10^{-21}	1300
	Ga	2.64×10^{-14}	1.14×10^{-14}	$1298 \longrightarrow 1373$

IV. CONCLUSION

In the present study, we have applied the SMM formalism to the calculations of the self-diffusion of GaAs semiconductor. We have found that both pre-exponential factor, D_0, activation energy, Q, and diffusion coefficient, D, of atoms Ga and As in GaAs crystal are increasing function of the temperature. The present formalism takes into account the higher-older anharmonic terms in the atomic displacements and it enables us to derive the diffusion coefficient of the atoms in semiconductors for a wide temperature range.

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